Imaging trace-element zoning in pyroxenes using synchrotron XRF mapping with the Maia detector array: Benefit of low-incident energy

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ABSTRACT

Trace-element zoning in igneous phenocrysts and cumulus phases is an informative record of magmatic evolution. The advent of microbeam X-ray fluorescence (XRF) mapping has allowed rapid chemical imaging of samples at thin section to decimeter scale, revealing such zoning patterns. Mapping with synchrotron radiation using multidetector arrays has proved especially effective, allowing entire thin sections to be imaged at micrometer-scale resolution in a matter of hours. The resolution of subtle minor element zoning, particularly in first-row transition metals, is greatly enhanced in synchrotron X-ray fluorescence microscopy (XFM) images by scanning with input beam energy below the FeKα line. In the examples shown here, from a phenocryst rich trachybasalt from Mt Etna (Italy) and from a Ni-Cu-PGE ore-bearing intrusion at Norilsk (Siberia), the zoning patterns revealed in this way record aspects of the crystallization history that are not readily evident from XFM images collected using higher incident energies and that cannot be obtained at comparable spatial resolutions by any other methods within reasonable scan times. This approach has considerable potential as a geochemical tool for investigating magmatic processes and is also likely to be applicable in a wide variety of other fields.

Keywords: Synchrotron, X-ray fluorescence mapping, pyroxene, zoning, Mt Etna, Norilsk

INTRODUCTION

Trace-element zoning patterns in igneous phenocrysts and cumulus minerals are useful recorders of magmatic histories within subvolcanic plumbing systems (Ubide and Kamber 2018). They have been used as evidence for supercooling (Mollo et al. 2013), multi-stage cooling histories (Ubide et al. 2019), crystal residence times in magmatic reservoirs (Costa and Morgan 2011; Lynn et al. 2018), and assimilation of country rocks in magmatic sulfide hosting intrusive systems (Barnes et al. 2016a; Mao et al. 2019). These patterns have been imaged by various different techniques including laser ablation–inductively coupled plasma mass spectrometry (LA-ICPMS) mapping (Ubide and Kamber 2018; Ubide et al. 2015, 2019), time-of-flight LA-ICP-TOFMS mapping (Ubide et al. 2019b), wavelength-dispersive electron microprobe mapping (Welsch et al. 2013), nanoscale secondary ion mass spectrometry (Nano-SIMS) (Seitz et al. 2018), and various techniques of microbeam X-ray fluorescence microscopy (XFM) (Barnes et al. 2016a, 2016b, 2018; Mao et al. 2019; Wang et al. 2019). The latter technique has been enhanced by the advent of the Maia multidetector array coupled with synchrotron microbeam sources (Paterson et al. 2011; Ryan et al. 2014a, 2014b). This combination of a multi-detector array and an ultra-bright collimated source enables a combination of high spatial resolution (~2 μm), sensitivity to concentrations in the hundreds to low thousands of parts per million range and rapid data collection, such that cm² areas can be scanned in a matter of a few hours. Numerous studies have revealed a range of types of trace-element distributions, not only in igneous minerals but also in a wide range of other geological and non-geological applications (Cleverley et al. 2012; Dyl et al. 2014; Ryan et al. 2014b; Fisher et al. 2015; Barnes et al. 2016b; Holwell et al. 2016).

Igneous pyroxenes are especially informative recorders of magmatic histories, in that they crystallize over a wide range of conditions and incorporate a range of elements with different geochemical characteristics into their crystal structure (Putirka 2017). Trace elements in individual pyroxene grains have been mapped by laser ablation–ICPMS in recent studies (Ubide et al. 2015, 2019; Ubide and Kamber 2018), which show the presence of sector zoning in Ti and oscillatory zoning in Cr in the same grain. These elements appear to be particularly susceptible to zoning on account of their relatively slow diffusion rates compared with divalent transition metals such as Ni and Mn (Cherniak et al. 2010).

Trace-element zoning in pyroxenes associated with magmatic sulfide ore deposits in ultramafic-mafic intrusions has been investigated using Maia detector based XFM at the Australian Synchrotron (Barnes et al. 2016b; Mao et al. 2019). As in the Mt Etna studies (Ubide et al. 2015, 2019; Ubide and Kamber 2018), the usually non-divalent elements Cr and Ti appear to be the most informative. Their non-divalent character results in slow diffusion rates, as it is necessary to break Si-Al bonds in the host pyroxene structure to accommodate charge balance. This property allows subtle zoning to be retained even in slowly cooled intrusions emplaced in the mid-crust (Taranovic et al. 2019). However, even with the benefits of the Maia-XFM method, effective detection limits...